Indian J. Phys. **77B** (6), 669-672 (2003)

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AN INTERNATIONAL JOURNAL

IJP B

Molecular interaction studies in the ternary mixture of 1-hexanol + acetonitrile + cyclohexane

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Received 14 February 2003, accepted 1 August 2003

Abstract The ultrasonic velocities, densities and viscosities have been measured in the ternary system of 1- hexanol + acetonitrile + cyclohexane at 303, 308 and 313 K. From these data, acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using the standard relations. The results have been analysed on the basis of variations in ultrasonic velocities and free lengths. It is observed that the addition of 1-ol leads to a compact structure. The presence of strong interactions are noticed in the ternary system. The peculiar behaviour of cyclohexane drastically influences the temperature variations.

Keywords : Ultrasonic velocity, acoustic parameters, dipolar and dispersive interactions.

PACS No. : 43.35.Bf

Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [1-3] as well as strongly interacting components [4-6]. Though a number of investigations have been carried out in liquid mixtures having alcohol as one of the components, ternary systems with 1-hexanol as one of the components has been scarcely reported. Further, ternary mixtures with alcohols as one component are indispensable for the industrial rectification column to avoid the formation of azeotropes. Hence, the authors have performed a thorough study on the interaction of 1- hexanol with the non-polar component cyclohexane and polar acetonitrile, using sound velocity data at different temperatures. The present work deals with the measurement of ultrasonic velocity and computation of related parameters in the ternary system of 1- hexanol + acetonitrile + cyclohexane at temperatures 303, 308 and 313 K.

The mixtures of various concentration in mole fraction were prepared by taking purified AR grade samples at 303 K. In all the mixtures, the mole fraction of the second component, acetonitrile ($x_2 = 0.3$), was kept fixed, while the mole fraction of the remaining two were varied from 0.0 to 0.7 so as to have the mixtures of different compositions.

The ultrasonic velocity (U) measurements have been made by a single frequency (2MHz) variable path interferometer with an accuracy of $\pm 0.1 ms^{-1}$. The density (ρ) measurements were made using a bicapillary pycknometer with an accuracy of 3 parts in 10^5 and 10 ml Ostwald viscometer is employed for viscosity (η) measurement, with an accuracy of $0.001 Nsm^{-2}$. The temperature has been maintained constant during the period of measurements by a water circulation system from the thermostat with a thermal stability of $\pm 0.1°C$.

Using the measured data, the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following standard expressions [7-10]:

$$\beta = (U^2 \rho) \quad (1)$$

$$L_f = K_T \beta \quad (2)$$

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$$V_f = \frac{M_{eff} U}{\eta K}^{3/2} \quad (3)$$

$$\pi_i = bRT\left(\frac{K_\eta}{U}\right)^{1/2} \frac{2/3}{M_{eff}^{7/6}} \quad (4)$$

$$A^E = A_{exp} - A_{id} \quad (5)$$

where K_T is a temperature dependent constant, having the values 199.5, 201.8, 203, X10^{-8} at 303K, 308K and 313K respectively, M_{eff} is the effective molecular weight $= \sum m_i x_i$, where x_i is the mole fraction and m_i is the molecular weight of i-th component, K is a constant independent of the temperature and nature of the liquid, equal to 4.28×10^9. b is the space filling factor being equal to 2 for all liquids and solutions, R is the universal gas constant.

The experimental values of density, viscosity and velocity at 303, 308 and 313 K for the pure components and for the system 1-hexanol + acetonitrile + cyclohexane are given in Table 1. The calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at different temperatures for the pure components and for the mixtures are presented in Table 2. The respective excess values at the said temperatures have been calculated and are shown in Figures 1 to 4.

It is found that the ultrasonic velocity increases with increasing concentration of 1-ol. An exactly reverse trend, as expected, is noticed in the variation of adiabatic compressibility As the number of hydrocarbon groups increase, the sound velocity is found to increase, as is evident from the Table 1. This behaviour, at such concentrations for the mixtures, which is different from the ideal mixture behaviour can be attributed to the intermolecular interaction in the system studied [11-14]

Table 1. Values of density(ρ), viscosity(η) and velocity (U).

Molefraction			ρ Kg m^{-3} Temperature K			η mNsm^{-2} Temperature			U ms^{-1} Temperature		
X_1			303	308	313	303	308	313	303	308	313
1 000	0.0	0.000	810.9	807 4	803 6	3 3450	3.0562	2 7538	1289 0	1276.3	1260 8
0 000	1.0	0 000	774 8	771 4	767.6	0 2992	0.2214	0 1873	1288 4	1267.9	1248 4
0.000	0.0	1 000	767 7	762 7	757 8	0 8003	0.7180	0 6673	1230 3	1212.5	1189 1
0.000	0.3	0 700	755 8	750.2	740.8	0 6625	0.6007	0.5603	1191.1	1172.6	1154 2
0.098	0.3	0 602	761 4	756.4	746.2	0.7086	0.6425	0 6024	1203 3	1186 4	1168 4
0.199	0 3	0.501	764 2	760.7	751 3	0.7525	0 6938	0 6422	1210 3	1192.6	1180 5
0.300	0.3	0 400	770 9	766 3	758 6	0 8028	0 7424	0.6935	1222 9	1206 6	1192 7
0.400	0.3	0 300	776 7	772.2	763.4	0.8421	0.7865	0.7446	1230.7	1216.4	1202 6
0.500	0 3	0 200	784.5	780 8	770 3	0.8981	0.8442	0.8032	1239 6	1225 3	1217 2
0.598	0.3	0 102	790 1	787 4	776.4	0.9509	0.9037	0.8684	1247 6	1237.6	1226.2
0.700	0 3	0 000	800 4	794 6	786.2	0 9975	0.9762	0 9346	1256 4	1249.2	1238 5

Table 2. Values of adiabatic compressibility(β), free length (L_f), free volume(V_f) and internal pressure(π_i).

Molefraction			β x10^{10} Pa^{-1} Temperature K			L_f x 10^{11} m Temperature K			V_f x 10^7 m^3 mol^{-1} Temperature K			π_i x 10^{-6} Pa Temperature K		
X_1	X_2	X_3	303	308	313	303	308	313	303	308	313	303	308	313
1 000	0.0	0.000	7.422	7.603	7 828	5 436	5.543	5.680	0.279	0 314	0.361	661	644	623
0.000	1.0	0.000	7.775	8.064	8 359	5 564	5 708	5.869	2.654	4.070	5.111	556	488	459
0.000	0.0	1.000	8.606	8.918	9.333	5 853	6.003	6.202	1 662	1.836	2.074	400	391	381
0.000	0.3	0.700	9.326	9.694	10 133	6.093	6.259	6.483	1.637	1.789	2.007	444	432	424
0.098	0.3	0.602	9.071	9.392	9.817	6.009	6.160	6.361	1.562	1.771	1 906	446	433	426
0 199	0 3	0.501	8 933	9 246	9.551	5.964	6.111	6.273	1.491	1 648	1.822	447	438	427
0 300	0.3	0.400	8.674	8 963	9 217	5.876	6.010	6.180	1 424	1.570	1.709	448	440	432
0 400	0 3	0.300	8.505	8.752	9 057	5.818	5.948	6.110	1.374	1.509	1.610	450	442	436
0.500	0.3	0 200	8 296	8.531	8.762	5.747	5.870	6.029	1.316	1.419	1.514	452	447	441
0.598	0.3	0 102	8 131	8.291	8.566	5 670	5.788	5.965	1.261	1.345	1.408	454	451	447
0.700	0.3	0.000	7.915	8.065	8.2923	5.611	5.708	5.911	1.226	1.255	1.322	456	457	454

However, the ultrasonic velocity decreases in all the cases as temperature is increased. The reverse trend is observed in the values of adiabatic compressibility.

As acetonitrile is having relatively a higher dielectric constant (∈ = 36) and being an electron donor than cyclohexane (∈=2.02) [15], the interaction between the molecules of acetonitrile with cyclohexane is found to be weaker than the interaction with primary alkanol. Dispersive type of interactions are expected between the primary alkanols and cyclohexane due to the non-polar nature of cyclohexane and its intertness towards electron donors [16] whereas dipole – dipole interactions or dipole–induced dipole interactions may arise between 1-hexanol and acetonitrile molecules, as acetonitrile are having permanent dipoles, due to asymmetric charge distribution in dissimilar molecules [17]. The addition of 1-ols with the mixture leads to a compact structure due to the presence of dipolar or dispersive type interactions.This contributes to a decrease in free length and hence compressibility. The regular fall in free length with the mole fraction of alkanol may be attributed to the close approach of the molecules [18].

According to Eyring and Kincaid [19], the regular fall in free length causes a rise in sound velocity in the mixture. This is also in accordance with the expected decrease in adiabatic compressibility following an increase in the sound velocity in all the mixture studied. Further, this trend is an indicative of clustering together of the molecules into some cage-like agglomerates due to associative effect of the polar group predominating over the other types of interactions [20].

From Table 2, it is noticed that as the concentration of 1-ol increases, free volume decreases whereas the internal pressure increases. This suggests the close packing of the molecules inside the shield, which may be brought about by the increasing magnitude of interactions [7,21].

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. The deviation of a physical property of the liquid mixtures from the ideal behaviour is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces [22].

The excess adiabatic compressibility (Figure 1) and the excess free length (Figure 2) are positive and continuously decrease with increasing 1-ol concentration . This is due to a weak bond of a type between a conventional localized hydrogen bond and the formation of charge transfer complex occurring between the components of the mixtures, as reported by Rowlinson [23]. The continuous decrease in excess free length, positive or negative, indicates the presence of specific interaction between the different sizes of molecules [13,22-24].

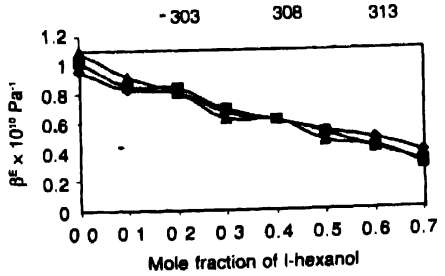

Figure 1. Mole fraction *vs* excess adiabatic compressibility.

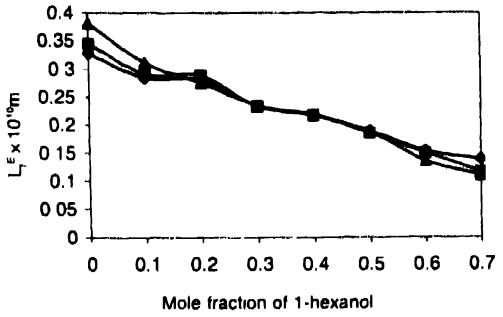

Figure 2. Mole fraction *vs* free length

However, as regards the temperature, the maximum β^E in ternary mixture is found to be shifted towards lower temperature with increasing 1-ol concentration. All the components are non-resonating, 1-ol and acetonitrile are having functional groups. But cyclohexane exhibits conformation from rigid chair form to flexible (boat) form and *vice - versa* [25]. As cited in our earlier work, the breaking up of hydrogen bonds are highly favoured in boat form and not so in chair form. Moreover, the relation between the standard free energy difference and equilibrium constant [26] reveals that the increase in temperature, supports the existence of cyclohexane in boat form. Literature [26]shows that both hydroxyl and methyl groups can form equatorial as well as axial mono/ di substituted cyclohexanes, the chances being higher for chair form. Further interactions can arise between these substituents,especially for axial [27], of the same or different cyclohexane molecules. Axial substituents can provide steric hindrance and equatorial are more stable[28]. At lower mole fractions of 1-ol (x_1 = 0.0,0.1), homogeneous mono or di-substituted equatorial methyl cyclohexanes are expected. As rise in temperature leads to rise in compressibility of mixture, maximum β^E is observed at 313K. However, at x_1 = 0.2,0.3 molefractions, heterogeneous equatorial di-substituted cyclohexanes are favoured at 303 K, because of their stability, that yields low β^E value. On increasing the temperature to 308 K, axial isomer formation may happen and by steric hindrance, β^E reaches maximum. But at 313 K, the crowding around the axial substituent is restricted and so, β^E value decreases again. Beyond 0.3 molefractions of 1-ol, relatively more number of alcohol clusters are available. The alcohol molecules in the pure state are arranged in homogeneous clusters of at least three molecules [29]. There are molecular size holes or voids in such liquid structures. The effect of temperature on these clusters will provide enormous voids [30] and thus the chance of formation of inert hydroxyl or methyl cyclohexane is enhanced. However, because of aforesaid reasons and as the component

compressibility increases by the favouring conditions boat cyclohexane, this results in low β^E at higher temperatures. Similar trends in β^E is also observed by Palaniappan in cyclohexane system. All these variations are reflected in the observed L_f^E.

The values of excess free volume (Figure. 3) are almost negative and increase with increase in concentration of 1-ol. This is due to the strengthening of dipolar interaction between the molecules of the mixture. It is interesting to note that the variation in the internal pressure values behave exactly in a reverse trend as that of free volume. Such a behaviour is also observed by Devinder Pal and Bhatti [31] in some ternary liquid mixtures. The weakening of dipolar interaction between the alcohol and halomethane by cyclohexane, has also been confirmed by the excess volume studies [32, 33]. The negative excess internal pressure in the mixtures at all concentrations clearly confirms this view.

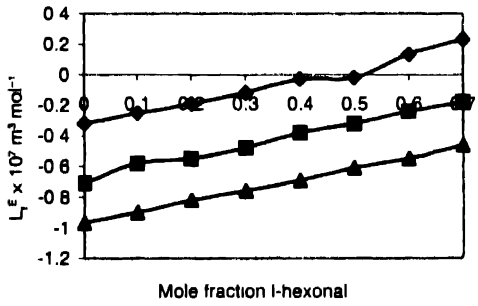

Figure 3. Mole fraction *vs* excess free volume.

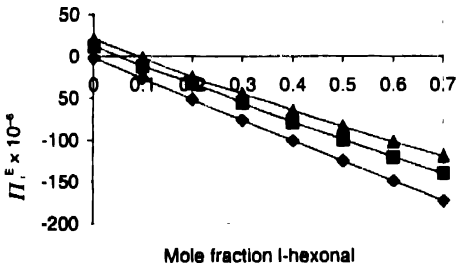

Figure 4. Mole fraction *vs* excess Internal pressure

Rferences

[1] S L Oswal, P Oswal and R P Phalak *J Sol Chem.* **27** 507 (1998)

[2] J Rajasekhar and P R Naidu *J Chem. Engg. Data* **41** 373 (1996)

[3] G Arul and L Palaniappan *J Acoust Soc. India* **28** 393 (2000)

[4] M Kalidoss and R Srinivasa moorthy *J. Pure. Appl. Ultrason.* **19** 9 (1997)

[5] J D Pandey and A K Shukla *J. Pure. Appl. Ultrason.* **19** 37 (1997)

[6] P S Nikam, T R Mahale and Mehdi Hasan *Indian J. Pure Appl. Phys* **37** 92 (1999)

[7] L Palaniappan *Ph. D. Thesis* (Annamalai University, India) (1998)

[8] B Jacobson *Acta. Chem. Scand.* **5** 1214 (1951)

[9] C V Suryanarayana and J Kuppusamy *J. Acoust. Soc. India* **4** 75 (1976)

[10] C V Suryanarayana and J Kuppusamy *J. Acoust Soc. India* **7** 131 (1979)

[11] A Sadasiva Rao, B Vijayakumar Naidu and K Chowdoji Rao *J Acoust Soc. India* **28** 303 (2000)

[12] K Tiwari, C Patra and V Chakravortty *Acoust Lett.* **19** 53 (1995)

[13] T N Srivastava and R P Singh *Acoust Lett* **6** 53 (1983)

[14] A N Kannappan and L Palaniappan *Indian J. Phys* **73B** 531 (1999)

[15] Moore and Styan *Trans. Faraday Soc.***52** 1556 (1956)

[16] L Palaniappan *Indian J Phys.* **75B** 515 (2001)

[17] A I Vogel *Practical Organic Chemistry* (London . Orient Longman) **4th** edn (1978)

[18] S Singh, N Prasad, R M Kushwah, K Sivanarayanana and S Prakash *Indian J. Pure Appl Phys* **18** 254 (1980)

[19] H Eyring and J F Kincaid *J Chem. Phys.* **6** 620 (1938)

[20] Surjit Singh Bhatti and Devinder Pal Singh *Indian J Pure Appl Phys* **21** 506 (1983)

[21] U Srinivasalu and P R Nadiu *J Pure Appl Ultrason* **17** 123 (1995)

[22] K C Reddy, S V Subrahamanyam and J Bhimsenachar *J. Phys. Soc Jpn.* **19** 559 (1964)

[23] J S Rowlinson *Liquids and Liquid Mixtures* (London · Butterworth) (1982)

[24] K Samatha, Srinivasa Rao and J Sree Ramamurthy *J Pure Appl Ultrason* **20** 5 (1998)

[25] D W A Sharp *Miall's Dictionary of Chemistry* (Longman Essex, UK) **5th** edn.(1981)

[26] Ernest L Eliel *Stereochemistry of Carbon Compounds* (New Delhi Tata McGraw-Hill) **9th** edn (1985)

[27] Ernest L Eliel and M Rerick *J. Am Chem. Soc* **82** 1367 (1960)

[28] C W Beckett, K S Pitzer and R Spitzer *J. Am Chem. Soc* **69** 2488 (1947)

[29] K Baba and K Kamiyoshi *Jpn J Appl Phys* **18** 1639 (1979)

[30] H D Bale, R E Shelper and D K Sorsen *Phys Chem Liquids* **1** 181 (1968)

[31] S Devinder Pal and S S Bhatti *J. Acoust Soc. India* **14** 39 (1986)

[32] R O Rastogi, J Nath and S S Dass *J Chem. Engg. Data* **22** 249 (1977)

[33] A Ali, A K Nain, V K Sharma and S Ahmad *J Acoust. Soc. India* **28** 287 (2000)